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Measurements of reactive chlorocarbons over the Surinam tropical rain forest: indications for strong biogenic emissions

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Abstract

Contrary to the understanding of the emissions and chemical behavior of halocarbons from anthropogenic sources (e.g. CFCs and HCFCs), the biogeochemistry of naturally emitted halocarbons is still poorly understood. We present measurements of chloromethane (methyl chloride, CH_3Cl), trichloromethane (chloroform, $CHCl_3$), dichloromethane (CH_2Cl_2), and tetrachloroethylene (C_2Cl_4) from air samples taken over the Surinam rainforest during the 1998 LBA/CLAIRE campaign. The samples were collected in stainless steel canisters on-board a Cessna Citation jet aircraft and analyzed in the laboratory using a gas chromatograph equipped with FID and ECD. The chlorocarbons we studied have atmospheric lifetimes of ~1 year or less, and appear to have significant emissions from natural sources including oceans, soils and vegetations, as well as biomass burning. These sources are primarily concentrated in the tropics (30° N–30° S). We detected an increase as a function of latitude of methyl chloride, chloroform, and tetrachloroethylene mixing ratios, in pristine air masses advected from the Atlantic Ocean toward the central Amazon. In the absence of significant biomass burning sources, we attribute this increase to biogenic emissions from the Surinam rainforest. From our measurements, we deduce fluxes from the Surinam rainforest of 7.6±1.8 μg CH_3Cl m^{-2} h^{-1}, 1.11±0.08 μg $CHCl_3$ m^{-2} h^{-1}, and 0.36±0.07 μg C_2Cl_4 m^{-2} h^{-1}. Extrapolated to a global scale, our emission estimates suggest a large potential source of 2 Tg CH_3Cl yr^{-1} from tropical forests, which could account for the net budget discrepancy (underestimation of sources), as indicated previously. In addition, our estimates suggest a potential emission of 57±17 Gg C_2Cl_4 yr^{-1} from tropical forest soils, equal to half of the currently missing C_2Cl_4 sources. We hypothesize that the extensive deforestation over the last two decades relates to the observed global downward trend of atmospheric methyl chloride.

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Reactive chlorocarbons over the Surinam tropical rainforest

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1. Introduction

The magnitude of natural sources in the global budgets of reactive organic chlorine species such as chloromethane (methyl chloride, CH_3Cl), dichloromethane (CH_2Cl_2), trichloromethane (chloroform, $CHCl_3$), and tetrachloroethylene (C_2Cl_4) is still poorly constrained (Khalil et al., 1999; Keene et al., 1999). These reactive organic chlorine species have an atmospheric lifetime from reaction with OH radicals of about 1.3 years for CH_3Cl, 0.5 years for $CHCl_3$, 0.4 years for CH_2Cl_2 and 0.3 years for C_2Cl_4 (Khalil, 1999). About 60% of the total emissions of reactive organic chlorocarbons (including chlorinated ethanes and ethenes) appear to be natural and concentrated in the tropics (Khalil, 1999; Keene et al., 1999). Although the atmospheric budget of reactive chlorocarbons (dominated by CH_3Cl) represents only about 15% of the total standing chlorine concentration, these compounds constitute the dominant source of reactive chlorine in the troposphere and lower stratosphere. An understanding of their present budget allows us to assess their role in atmospheric chemistry in the past, in the absence of anthropogenic chlorine sources, and in the future after anthropogenic chlorine has decreased significantly.

The most prominent organic chlorine species is CH_3Cl with a present mean background concentration of ~550 pptv (pptv = mol^{-12} mol) in the extra-tropics and ~600 pptv in the tropics (Lee-Taylor et al., 2001; Scheeren et al., 2002, 2003; Montzka et al., 2003). CH_3Cl is removed from the atmosphere mainly by reaction with the OH radical (3.43 Tg yr^{-1}), and to a lesser extend by reaction with Cl radicals in the marine boundary layer (0.20 Tg yr^{-1}), microbial degradation in soils (0.18 Tg yr^{-1}), loss to polar oceans (0.075 Tg yr^{-1}), and loss to the stratosphere (0.20 Tg yr^{-1}) (Montzka et al., 2003). In the stratosphere CH_3Cl contributes to about 17% of present chlorine catalyzed ozone destruction (Harper, 2000). Within a fair degree of uncertainty, about half of the estimated annual global sink of 4 Tg CH_3Cl has been accounted for, mainly by emissions from the oceans and biomass burning (Lobert et al., 1999; Lee-Taylor et al., 2001; Montzka et al., 2003). The search for new CH_3Cl sources has resulted in the

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identification of emission fluxes from wetlands (Varner et al., 1999), peat land (Dimmer et al., 2001), coastal waters (Li et al., 1999), coastal salt marshes (Rhew et al., 2000; Bill et al., 2002), and from forest soils (Dimmer et al., 2001). These emission fluxes, however, are to small to account for the large discrepancy between known sources and the estimated global sink. Recently, several studies have pointed to higher plants as potential major source of CH_3Cl to the atmosphere (Lobert et al., 1999; Khalil et al., 1999; Harper, 2000, Yokouchi et al., 2000). The emission of CH_3Cl from higher plants (potato tubers) was first reported by Varns (1982) and later in a laboratory study by Saini et al. (1995), involving herbaceous species and halophytes. Recent observations by Yokouchi et al. (2002), supported by a model study by Lee-Taylor et al. (2001), point to large fluxes of CH_3Cl from tropical vegetation. Lee-Taylor et al. (2001) show that observed mixing ratios and latitudinal distributions are best reproduced in their model by addition of a large tropical terrestrial CH_3Cl source of the order of 2.3 $Gg\,yr^{-1}$, indicating that tropical plants might the largest known source.

Besides the search for new CH_3Cl sources, there has been a considerable effort to identify and quantify natural sources of the reactive chlorocarbons $CHCl_3$, CH_2Cl_2 and C_2Cl_4 to decrease considerable uncertainties in their global budgets. The atmospheric budget of $CHCl_3$ appears to be dominated by natural emissions from the oceans, responsible for more than half of the known source budget (Keene et al., 1999). Furthermore, there have been extensive studies pointing to significant $CHCl_3$ fluxes from forest soils related to bio-degradation processes involving fungi (Watling and Harper, 1998; Hoekstra et al., 1998, 2001; Haselmann et al., 2000a, 2000b). In addition, natural emissions of $CHCl_3$ have been reported from peat land (Dimmer et al., 2001), and from biomass burning (Rudolph et al., 1995; Scheeren et al., 2002). The known source budgets of CH_2Cl_2 and C_2Cl_4, on the other hand, are for ~70% and ~90% determined by industrial emissions (Khalil et al., 1999; McCulloch et al., 1999). Natural sources include CH_2Cl_2 and C_2Cl_4 emissions from the oceans (Keene et al., 1999, and references therein), and CH_2Cl_2 emissions from biomass burning (Rudolph et al., 1995; Scheeren et al., 2002). Moreover, Hoekstra et al. (2001) observed a small soil flux of

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C_2Cl_4 in Douglas fir forest. To our knowledge, there have been no reports of terrestrial biogenic emissions of CH_2Cl_2. For an extensive review of biogenic formation and degradation processes of organohalogens, not discussed here, we would like to refer to a recent special issue in Chemosphere (2003).

This paper presents measurements of reactive chlorocarbons from air samples collected over the rainforest of Surinam, South America, as part of the Large-Scale Biosphere-Atmosphere Experiment in Amazonia Co-operative LBA airborne regional experiment (LBA/CLAIRE) in March 1998. The air samples were collected during 10 measurement flights conducted from Zanderij airport in Surinam (5.4° N–55.2° W) using a Cessna Citation II aircraft operated by the Delft University of Technology. The flights covered an area roughly between 2° N –7° N and 53° N–59° W at altitudes ranging from 50 to 12 500 m. The measurement payload provided in situ observations of ozone (O_3), carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), organic tracer species (notably, acetone (CH_3COCH_3), isoprene, and acetonitrile (CH_3CN)), and aerosols. In total, 80 air samples were collected for laboratory analyses on non-methane hydrocarbons (NMHC) and chlorocarbons. Detailed analyses of the trace gas distributions of acetone, isoprene, CO and CO_2 during LBA/CLAIRE have been reported by Pöschl et al. (2001), Warneke et al. (2001), and Williams et al. (2001b), respectively. Part of the NMHC results has been included in a study on the variability-lifetime relationship of organic trace gases by Williams et al. (2001a), and in a study focusing on a high altitude biomass burning plume by Andreae et al. (2001). Here, we focus on measurements of the chlorocarbons CH_3Cl, CH_2Cl_2, $CHCl_3$, and C_2Cl_4, which have been analyzed in concurrence with measurements of NMHC, CO, and acetonitrile over the Surinam rainforest.

Apart from the coastal region were the majority of the population of about 400.000 people resides, Surinam is covered by pristine Amazonian rain forest. Hence, our chlorocarbons measurements provide new information on the role of tropical rain forest ecosystems as natural source of chlorocarbons to the atmosphere. The measurements are used to estimate fluxes of chlorocarbons from the Surinam tropical rainforest, and to

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estimate global annual mean emission fluxes from tropical rain forest ecosystems. Finally, we discuss the relationship between observed decreasing trends in atmospheric CH_3Cl and global tropical forest cover over the last two decades.

2. Measurement techniques

The measurement techniques employed in this study have all been described in detail elsewhere. Here, we briefly summarize the methods, their precision and accuracy.

CO was measured by an airborne Tunable Diode Laser Spectrometer (TDLAS) developed and operated by the Max Planck Institute in Mainz, Germany (Wienhold et al., 1998; Williams et al., 2001b). CO was detected at 1 Hz with an accuracy of ±3% and precision of ±2%.

Acetone and acetonitrile were detected by an airborne Proton-Transfer-Reaction Mass-Spectrometer (PTR-MS), which was developed operated by Innsbruck University (Lindinger et al., 1998; Crutzen et al., 2000). About 10 masses (including acetone and acetonitrile) could be identified at a time resolution of 10 s. For a detailed interpretation of mass scans obtained over the Surinam rainforest we refer to Williams et al. (2001c). The detection limit was 0.4 ppbv for acetone and 0.2 ppbv for acetonitrile. The measurement accuracy was better than ±30%, while the precision was typically ±20% for acetone and ±30% for acetonitrile.

A total of 80 whole air samples were collected in stainless steel canisters between 0.1 to 12.5 km altitude for subsequent laboratory analysis of hydrocarbons and chlorocarbons by a Gas Chromatograph equipped with a Flame Ionization and Electron Capture Detector (GC-FID/ECD). For technical details of the GC-method we refer to Williams et al. (2001a) and Scheeren et al. (2002). The accuracy based on commercial gravimetrically prepared standard mixtures (PRAXAIR) was ±3% for hydrocarbons and ±2% for chlorocarbons. The precision for hydrocarbons > 15 pptv used in this study was 11% for acetylene (C_2H_2), 5% for propane (C_3H_8), 7% for n-butane (n-C_4H_{10}), 6% for benzene (C_6H_6). The precision for chlorocarbons was 4% for CH_3Cl, 11% for

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CH_2Cl_2, 5% for $CHCl_3$, and 7% for C_2Cl_4.

3. Meteorology

During the short dry season from February to April, Surinam lies in the northern meteorological hemisphere with the Inter Tropical Convergence Zone (ITCZ) located at a few degrees south. The (short) dry season is generally characterized by low precipitation due to strong subsidence over the region suppressing deep convective activity. March 1998 was a particularly dry month due to the "El Niño" phenomenon. Northeasterly trade winds carry pristine air masses from the Atlantic Ocean land over the tropical rainforest towards the ITCZ, allowing primary organic emissions and their oxidation products to accumulate.

During the day, a dry convective boundary layer is formed, coupling the rainforest canopy to the atmosphere above through turbulent mixing. This layer is referred to as the mixing layer, where emissions from the rainforest build-up. In contrast to the marine conditions, the boundary layer over land has a distinct diurnal cycle driven by solar heating during the day and surface radiative cooling during the night. During night, the daytime mixing layer is decoupled from the surface by a strong temperature inversion. After dawn, the shallow nocturnal mixing layer starts to grow via turbulent mixing, reaching a maximum depth around 1500 m in the afternoon during the dry season (Martin et al., 1988). A shallow convective cloud layer forms above the mixing layer in the course of the day. The convective clouds transport air between the mixing layer and the convective cloud layer. The shallow convective cloud tops generally coincide with the top of the trade wind inversion, which acts as a barrier to mass transport out of the boundary layer to the free troposphere (Martin et al., 1988; Zimmerman et al., 1988).

The typical evolution of the mixed layer height over the Amazon tropical rainforest during the dry season is shown in Fig. 1. The diurnal pattern has been composed from observed temperature inversions in potential temperature profiles from the 1985

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Amazon Boundary Layer Experiment (ABLE 2A) (Martin et al., 1988) and from profiles obtained from ascent and descent with the Citation aircraft during LBA/CLAIRE (Krejci et al., 2003). It was found that the depth of the mixing layer during LBA/CLAIRE reached an altitude between 1300 to 1700 m at midday (depicted as a gray band in Fig. 1) in good agreement with the ABLE 2A observations.

Deep convection in the ITCZ brings boundary layer (BL) air masses into the middle and upper troposphere, where they can be caught in a southerly return flow. Indeed, outflow from the ITCZ has been clearly observed in the middle troposphere on 19, 21, and 29 March which will be discussed in the next section, and on 26 March, which has been described in detail by Andreae et al. (2001).

The mean observed north-south wind component for all flights, expressed as the cosine of the wind angle multiplied by the observed wind speed is shown in Fig. 2 (running mean over 1278 points; negative values indicate southerly winds). Northeasterly trade winds prevailed up to about 2.5 km altitude. Southerly winds were generally observed in the free troposphere (FT) between 2.5 and 4 km, 5.5 and 8 km, and between 8 and 12 km relating to ITCZ outflow. For more details about the meteorology during LBA/CLAIRE we refer to Williams et al. (2001b) and Krejci et al. (2003).

4. Results

4.1. Vertical distributions

Before we focus on the boundary layer measurements we present a general overview of the vertical distributions of chlorocarbons and selected combustion tracers measured simultaneously during March 1998. As such, we show vertical concentration profiles (in pptv) of the reactive chlorocarbons CH_3Cl, CH_2Cl_2, $CHCl_3$, and C_2Cl_4 as detected in all canister samples (80) collected during March 1998 in Fig. 3a. In Fig. 3b, profiles of the combustion tracers CO and CH_3CN from in situ measurements, as well as the hydrocarbons acetylene, propane and benzene from the canisters are shown. The CO and

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CH_3CN data are averaged time series corresponding with the duration of the canister sampling (~1–3 min). Error bars in Fig. 3 denote the measurement uncertainty, which is larger than the 1σ standard deviation of the mean for CO and CH_3CN. Enhanced CO and hydrocarbons (notably acetylene and propane), in combination with enhanced concentrations of the biomass burning tracer CH_3CN (Holzinger et al., 1999; Lobert et al., 1990), point to the influence of biomass burning emissions. Elevated concentrations of benzene from fossil fuel use and of C_2Cl_4 from industrial use (a degreasing agent used notably in dry cleaning) are related to urban/industrial pollution. The flights in which the highest tracer concentrations have been observed in the FT between 8 and 12 km altitude are color-coded in Fig. 3, being flight 4 in black (19 March), flight 5 in blue (21 March) flight 8 in green (26 March) and flight 10 in red (29 March). In addition to the vertical profiles, an overview of average and median mixing ratios of all air samples collected below 2 km in the mixing layer, between 2–7 km in the lower free troposphere (LT), and above 7 km in the middle free troposphere (MT) is presented in Table 1.

Figure 3 and the results in Table 1 demonstrate that besides the boundary layer, the highest mixing ratios (except for CH_2Cl_2 and $CHCl_3$) have been observed above 7 km in the MT, whereas the LT shows a minimum. Moreover, the results in Table 1 show that in the case of C_2H_2 and C_6H_6, the UT was significantly more polluted than the lower atmosphere, emphasizing the minor role of local pollution sources. This MT maximum in hydrocarbons, notably of benzene with a relatively short photochemical lifetime of a week or less, points to rapid uplifting of polluted air masses into the MT. The vertical wind profile in Fig. 2 indicates that the MT airflow was predominantly southerly, originating over the region where the ITCZ was active. Hence, the most likely transport mechanism is deep convection and subsequent outflow of boundary layer air into the MT associated with the ITCZ. Meteorological evidence of ITCZ outflow encountered in the MT is provided by 10-day backward trajectory analysis presented in Fig. 4. The back-trajectories, calculated by the Royal Netherlands Meteorological Institute (KNMI), are based on 6-hour averaged 3-D wind field from the European Centre for Medium-

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range Weather Forecast (ECMWF) (Stohl et al., 2001). Every 2 min along the flight track a back-trajectory was computed. Figure 4 shows a selection of back-trajectories along the MT flight tracks where the highest tracer concentrations have been observed. In black we show back-trajectories starting on 19 March (flight 4) between altitudes of 10–12 km, in blue trajectories starting on 21 March (flight 5) between 8–9 km, and in red trajectories starting on 29 March (flight 10) between 9–12 km. The ITCZ, denoted by the gray band in Fig. 4, was located at about 5° S of the Guyana's based on GOES satellite visible and infrared images of March 1998 (http://www.satmos.meteo.fr). The back-trajectories analysis depicted in Fig. 4, clearly reveals the occurrence of rapid upward transport of lower tropospheric and boundary layer air into the upper troposphere (8–12 km altitude) over central to northwestern Brazil in the ITCZ region, 3 to 9 days prior to the flights.

The enhancements of C_2Cl_4, C_2H_2 and C_6H_6 on 19 March (flight 4), as well as high CO, C_2H_2 and C_3H_8 encountered in the MT on 21 March (flight 5), suggest a strong influence of anthropogenic pollution, which appears to originate over the populated northwestern coastal region of Brazil (Fig. 4, black and blue trajectories). The peak at about 11 km altitude observed on 26 March (flight 8), notably of CO, CH_3CN and CH_3Cl is a strong signature of biomass burning. This event was related to large savanna/forest fires that took place near the Brazil/Venezuela border and is described in detail by Andreae et al. (2001). Finally, on 29 March (flight 10) high CH_3Cl mixing ratios (>700 pptv) have been observed at an altitude of 11–12 km in the absence of enhanced combustion tracers (e.g. C_2H_2, CH_3CN), pointing to a strong natural source. Here, the back-trajectory analysis suggests an air mass origin over the pristine rainforest of central Amazonia. In the next section, we focus on chlorocarbon gradients in the mixing layer as observed over the pristine Surinam rainforest.

4.2. Accumulation of chlorocarbons in the mixing layer

Yokouchi et al. (2002) showed that tropical plants emit significant amounts of CH_3Cl, while others have reported forest soil emissions of $CHCl_3$ (e.g. Watling and Harper,

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1998) and possibly that of C_2Cl_4 (Hoekstra et al., 2001). Here we investigate the latitudinal gradients of chlorocarbons in the mixing layer over the Surinam tropical rainforest to assess the biogenic sources. To do so, we investigated the relationship between observed chlorocarbons mixing ratios and the time the encountered air masses spend in the mixing layer over the Surinam rainforest while moving into a southeasterly direction, referred to as the Forest Contact Time (FCT). The FCT, defined as the time (in hours) an air parcel spends in the mixing layer starting from the coast the coast (6° N) towards the Brazilian border (2° N), was determined as following:

$$FCT = \Delta L / \cos(WA) \times WS / 3600 \quad (1)$$

where ΔL is the latitudinal distance from the coast (m); cos(WA) is the cosine of the mean wind angle (WA) taken from the aircraft measurement along the boundary layer flight track; WS is the mean wind speed in the boundary layer from the aircraft measurement (m s^{-1}). The average wind angle and wind speed of all boundary layer flight legs was 45±13° and 10±3 m s^{-1}.

A significant linear relationship between the trace gas concentrations and the FCT of the encountered air masses can point to biogenic sources. Hence, the slope of a linear regression analysis, ΔC/ΔFCT, can be used to estimate fluxes. First, however, the mixing layer data set was screened for possible influences of local pollution sources such as biomass burning or of anthropogenic origin. CH_3Cl and to a lesser extend $CHCl_3$ are emitted from biomass burning (Lobert et al., 1999), while CH_2Cl_2 and C_2Cl_4 have urban-industrial sources (Keene et al., 1999). Therefore, air samples affected by emissions from biomass burning, anthropogenic combustion processes, or urban/industrial activities were excluded since they can contain enhanced chlorocarbon concentrations. We note that apart from some isolated small biomass burning events encountered on 15 and 26 March, there were no indications of widespread fire activity in Surinam during course of the campaign (Williams et al., 2001b). Nevertheless, we decided to reject an air sample when the C_2H_2 and C_6H_6 and/or CH_3CN mixing ratios exceeded twice their "background" value, as detected over the ocean of ~50, ~30 and ~150 pptv

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and/or CO exceeded 140 ppbv, based on a study by Williams et al. (2001b). In addition, we selected only daytime observations after 10:00 local time to avoid effects from the break-up of the nocturnal boundary layer in the early morning. Emissions from the rainforest (or other ground sources) accumulate in the shallow nocturnal boundary layer (Zimmerman et al., 1988). During dawn the nocturnal BL breaks up, which can cause a temporarily peak in the concentrations of the accumulated species.

After applying the selection criteria to exclude other potential sources than biogenic, a total of 27 air samples in the mixing layer over the Surinam rainforest remained. The selected air samples were collected between 10:30 and 17:30 local time at altitudes between 96 and 1070 m. The geographical distribution of the air samples collected in the Surinam mixing layer is depicted in Fig. 5. It shows that the data represent an area spanning ~500 km of pristine tropical rainforest from the Atlantic coast to the Brazilian border.

In Fig. 6 the concentrations of combustion species (Fig. 6a) and chlorocarbons (Fig. 6b) from the selected air samples are shown as a function of FCT. The correlation coefficient r (at the 95% confidence level) indicates the significance of the linear relationship. Figure 6a shows that the combustion tracers C_2H_2, C_6H_6 and CH_3CN have no significant relationship with the FCT, clearly demonstrating that biomass burning or other non-biogenic sources were negligible. CO, on the other hand, shows a significant positive trend with increasing FCT. An important source of CO over the tropical rainforest, apart from biomass burning, is the oxidation of isoprene and terpenes emitted by vegetation (Zimmerman et al., 1988). According to Williams et al. (2001b) isoprene oxidation resulted in a net increase of 29 pptv CO km^{-1} over the Surinam rainforest during March 1998. Our selection of CO data shows a similar increase of ~23±3 pptv km^{-1}, close to the result of Williams et al. (2001b). Thus, we can attribute the CO increase as a function of FCT to the oxidation of biogenic hydrocarbons, in particular isoprene.

In Fig. 6b we show that there is a significant linear relation ($r > 0.5$ at the 95% confidence limit) between the atmospheric concentration of CH_3Cl and $CHCl_3$ and the FCT.

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When we exclude an outlier in the C_2Cl_4 data, we find a small but significant increase of C_2Cl_4 over the Surinam rainforest as well. There are no indications of an emission flux of CH_2Cl_2. In the absence of significant biomass burning or urban/industrial sources we attribute the positive gradients of CH_3Cl, $CHCl_3$, C_2Cl_4 to biogenic emissions from the tropical rainforest ecosystem. Note that we use the term "ecosystem" because it is difficult to differentiate between the various biogenic sources, such as direct emissions from vegetation or microbiological activity in the forest soil. However, based on present knowledge the enhancement of CH_3Cl is most likely related to emissions from tropical vegetation (e.g. Yokouchi et al., 2002), whereas the $CHCl_3$ and C_2Cl_4 emissions are predominantly related to the biological decay of organic material in the forest soil (e.g. Hoekstra et al., 2001).

To determine the slope, $\Delta C/\Delta FCT$, of the relationship between the chlorocarbon mixing ratio and the FCT, a least-squares linear regression analysis was performed allowing precision errors in both the x- and the y-variable (linear fit in Fig. 6b). The estimated error in the FCT was ~10%, while precision errors of 4% for CH_3Cl, 5% for $CHCl_3$ and 7% for C_2Cl_4 were applied. This linear regression technique, described by Press et al. (1992) is referred to as an orthogonal distance regression (ODR) analysis. The results and uncertainty of the ODR analysis are summarized in Table 2. The relative uncertainties in the $\Delta C/\Delta FCT$ are 23% for CH_3Cl, 7% for $CHCl_3$ and 16% for C_2Cl_4. In the next section we use the $\Delta C/\Delta FCT$ values to estimate chlorocarbon fluxes from the tropical rainforest.

5. Chlorocarbon emission fluxes from the tropical rainforest

5.1. Flux calculation method

The flux, F, in g m^{-2} h^{-1} of a chlorocarbon out of the rainforest at the top of the mixing layer was estimated using the linear regression slope, $\Delta C/\Delta FCT$ in mol mol^{-1} h^{-1}, of

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the chlorocarbons in the following equation:

$$F = \Delta C/\Delta FCT \times L_{ml} \times (p \times M/R \times T), \quad (2)$$

where L_{ml} is the mean mixing layer height (m); p is the mean air pressure; M is the molecular weight of the chlorocarbon (g); $R = 0.08314$ is the gas constant (hPa m^3 K^{-1}); T is the mean air temperature (K) in the mixing layer. This simple flux estimate can be applied assuming a well mixed mixing layer of a constant height, a negligible loss out of the mixing layer over the course of a day, and assuming a homogeneous flux out of the forest canopy.

5.2. Fluxes of CH_3Cl, $CHCl_3$, and C_2Cl_4

The evolution of the mixing layer height during a typical day in March 1998 over the Surinam rainforest was shown in Fig. 1. The data selection used to calculate the ΔC/ΔFCT corresponds to a local time between 10:30–17:30 h. Based on typical diurnal mixing layer heights observed over the Amazon rainforest (Fig. 1), we deduce a mean mixing height of ∼1.5 (±0.2) km, corresponding to the times of the selected observations. Applying a mean BL-height of 1.5 km, a mean temperature of 298 K, a mean pressure of 950 hPa, and the calculated ΔC/ΔFCT values (Table 2) in Eq. (2), we derive fluxes in μg m^{-2} h^{-1} of 7.6±1.8 for CH_3Cl, 1.11±0.08 for $CHCl_3$ and of 0.36±0.07 for C_2Cl_4.

The accuracy of the flux estimate is dependent on the uncertainty in the ΔC/ΔFCT emission factors, the variability in the mixing layer height, and the assumption of a homogeneous well mixed mixing layer with minimum losses at the top. Errors induced by inhomogeneous conditions in the mixing layer are incorporated in the uncertainty of the calculated ΔC/ΔFCT values (Sect. 4.2). The uncertainties in the emission factors and mixing layer height add up to ∼35% for CH_3Cl, ∼20% for $CHCl_3$, and to ∼30% for C_2Cl_4. To get a first indication of possible losses at the top of the mixing layer due to convective mixing, we used a single column model version of the ECHAM4

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chemistry-climate model (Ganzeveld et al., 2002). The model was run with meteorological conditions representative for the Surinam dry season and a homogeneous CH_3Cl canopy flux. Running the model without convective mixing (no shallow cumulus layer), it appeared that losses due to turbulent fluxes at the top of the mixing layer are negligible. However, when convective mixing was included in the model, losses at the top of the mixing layer could become as large as −25% in the afternoon. This estimate provides a first indication that losses could be between 0% and −25% over the course of a day, depending on the intensity of convective mixing. Clearly, a more detailed sensitivity analysis, which is beyond the scope of this study, would be necessary to quantify the role of convective mixing more accurately. Hence, compensating for losses at the top of the mixing layer would increase our flux estimates. Thus, our estimates can be considered as lower limits.

The flux estimates are summarized in Table 3 and can be compared to flux estimates for forest sites from other studies. We find a remarkably good agreement, in light of the uncertainties, with other flux estimates of CH_3Cl, notably with that of Yokouchi et al. (2002) for tropical vegetation. For $CHCl_3$ our estimate lies at the low-end of other flux estimates ranging from 0.1 to 53 μg m^{-2} h^{-1}. Our flux estimate of C_2Cl_4 is, to our knowledge, the first estimate of emissions from tropical vegetation. It is more than an order of magnitude higher than the median value of 0.022 μg m^{-2} h^{-1} observed above Dutch Douglas fir forest soil by Hoeksta et al. (2001). In agreement with our finding, there have been no reports, to our knowledge, of biogenic land-based emissions of CH_2Cl_2.

5.3. Global chlorocarbon emission fluxes from tropical forest

We applied the chlorocarbon flux estimates for the Surinam rainforest to obtain a global annual emission estimate from tropical rainforest. According to Yokouchi et al. (2002), we can assume a constant emission flux of CH_3Cl from tropical plants independent of the time of day. This also implies a low seasonal variability when evergreen tropical plants are a major tropospheric source. Indeed, the observed seasonal cycle ampli-

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tude decreases with latitude and is less than 5% (of the yearly mean) in the tropical regions for CH_3Cl (Khalil and Rasmussen, 1999). It appears to be largely driven by the variability in the OH radical concentration and the enhanced biomass burning occurring during the dry seasons in the tropics. Therefore, for the estimates of annual emissions from tropical rainforest we assumed a seasonally independent flux.

Another factor of to be considered is the role of soil salinity (or the availability of chlorine to biogenic chlorocarbon metabolism). There are indications that a high soil salinity (Cl^- content) enhances biosynthesis and subsequent emissions of CH_3Cl from fungi and higher plants (Harper, 2000). In addition, model simulations by Lee-Taylor et al. (2001) suggest that tropical coastal and near-coast CH_3Cl emissions may be more important than those further inland, dependent on the deposition of sea salt containing aerosol. Although not apparent in our Surinam rainforest gradients, this implies that the estimated fluxes for the Surinam rainforest may be enhanced relative to fluxes from the rainforest deeper into the Amazon. During the LBA-CLAIRE 1998 campaign, Formenti et al. (2002) observed advection of Saharan dust at two sites in Surinam (Zanderij airport, 55.47° N, 55.12° W, and Sipaliwini, 2.12° N–56.06° W) and a site in Brazil (Albina, 1.55° S, 59.24° W), at more than 800 km inland. They found that the wet and dry deposition of Saharan dust to the rainforest ecosystem is an important source of sea salt elements (Na, Cl, S), beside crustal dust elements (e.g. Al, Si, Ca, Fe). It was shown that maritime air significantly contributed to the concentrations of Cl in aerosol samples collected at Balbina. The results of Formenti et al. (2001) corroborate earlier work by Artaxo et al. (1995), concluding that the transport of sea salt aerosol, embedded in dust plumes transported at low altitudes, is responsible for excess Cl soil concentrations observed deep into the Amazon basin. Hence, we assume that soil salinity is not a limiting factor for global biogenic chlorocarbon production.

To obtain annual fluxes in Gg yr^{-1} of CH_3Cl, $CHCl_3$ and C_2Cl_4 from tropical rainforests we used the following equation:

$$\text{Annual flux} = \text{Surinam flux} \times \text{Emission period} \times \text{Forest cover area}, \quad (3)$$

where the "Surinam flux" is the flux estimate obtained for the Surinam rainforest (in μg

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m^{-2} h^{-1}); the "Emission period" is the amount of emission hours per year (365 × 24 h for the evergreen tropical forest); the "Forest cover area" estimates were adopted from the latest FAO Forest Resource Assessment 2000 report (FAO, 2001) being 8.158 × 10^{12} m^2 for the Amazon region, 2.704 × 10^{12} m^2 of Asian tropical forest and 7.258 × 10^{12} m^2 for the remaining tropical forest (mainly Africa).

About half of the Asian tropical forest is lowland tropical forest, which is different from Asian highland tropical forest in terms of vegetation composition (Yokouchi et al., 2002). Asian lowland tropical forest constitutes for about a third of certain types of ferns and tropical plants from the Dipterocarpaceae family, which can emit considerable amounts of CH_3Cl (Yokouchi et al., 2002). They performed a study on CH_3Cl emissions from a wide range of Asian tropical plants in a glasshouse, from which they estimated a CH_3Cl flux from Dipterocarpaceae in southeast Asian lowland tropical forest of 0.91 Tg yr^{-1} based on 1997 FAO forest cover estimates. Using the latest FAO 2000 tropical forest cover estimates (FAO, 2001), this flux estimate becomes 0.88 Tg yr^{-1}. When we apply the Surinam emission factor to estimate a yearly flux of CH_3Cl from the remaining fraction of Asian (highland) tropical forest this yields an additional flux 0.09 Tg yr^{-1}.

Summing up, we find a total global emission of 2 Tg CH_3Cl per year from (sub)tropical vegetation, which is more than sufficient (within the uncertainty of the estimates) to account for the total of missing sources and to close the global tropospheric budget. Our estimates are in good agreement with the model study by Lee-Taylor et al. (2001), who found that observed mixing ratios are best reproduced by addition of a large tropical terrestrial source of ~2.3 Tg, which includes 0.18 Gg yr^{-1} redistributed from Asian biomass burning emissions. Interestingly, the latter is in conflict with new estimates of biomass burning emissions of CH_3Cl from the use of biofuels in Southeast Asia by Scheeren et al. (2002). They find that CH_3Cl emissions from the use of biofuels could be underestimated by 30–35% (~0.28 Gg yr^{-1}) for India and Southeast Asia based on measurements performed over the Indian Ocean during the INDOEX 1999 experiment. These conflicting estimates illustrate the level of uncertainty still present in quantifying the major CH_3Cl sources.

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Our estimates of annual fluxes of $CHCl_3$ from global tropical forest of 175±35 Gg yr^{-1} (based on the Surinam emission flux) and a flux from temperate forest of ~5 Gg yr^{-1} (based on a forest soil flux of 0.033 μg m^{-2} h^{-1} from Haselmann et al. (2000a) and temperate forest cover of 1.881×10^{13} m^2 from FAO, 2001) combine to 180±35 Gg yr^{-1}. This number compares well to the ~200 Gg yr^{-1} from (forest) soil emissions estimated by Khalil et al. (1999), which are mainly concentrated in the tropics. Extrapolating the Surinam rainforest C_2Cl_4 flux onto a global scale, we can estimate a total flux from tropical forests of 57±17 Gg yr^{-1}. This flux could account for almost half of the amount of missing C_2Cl_4 sources (~128 Gg yr^{-1}) in the global budget by Keene et al. (1999).

5.4. Global emission budgets of CH_3Cl, $CHCl_3$, and C_2Cl_4

In Table 4 we summarize our flux estimates for tropical rainforests and include emission flux estimates from the literature of the oceans, biomass burning, industrial sources and other newly identified biogenic sources. As such, an overview is given of the global annual source budgets of CH_3Cl, $CHCl_3$, and C_2Cl_4 in Tg yr^{-1}. CH_2Cl_2 is not included here because it has no terrestrial biogenic sources. Wiedman et al. (1994) was able to model the global distribution of C_2Cl_4 consistently without biogenic input. However, the uncertainty in the global budget remains to be large (Keene et al., 1999) and allows for the inclusion of newly identified natural sources. In addition to Table 4, the composition of global source budgets of CH_3Cl, $CHCl_3$, and C_2Cl_4 is illustrated in pie-plots in Fig. 7. Note that an annual emission flux of 128 Gg CH_3Cl yr^{-1} from fungal (soil) activity (Lee-Taylor et al., 2001) has not been included, because we consider this to be incorporated in the fluxes from tropical forest ecosystems. We adopted annual global net flux estimates from the oceans of 477 Gg CH_3Cl yr^{-1} from Lee-Taylor et al. (2001), and 359 Gg $CHCl_3$ yr^{-1} and 19 Gg C_2Cl_4 yr^{-1} from Khalil et al. (1999). A small flux of 3.6 Gg C_2Cl_4 yr^{-1} and 5.4 Gg $CHCl_3$ yr^{-1} was estimated for the global temperate forest (FAO, 2001) using the mean C_2Cl_4 forest soil flux measured by Hoekstra et al. (2001) and the mean $CHCl_3$ forest soil flux from Haselmann et al. (2000a), respectively.

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Recently identified biogenic global source fluxes included in Table 4 are 170 (65–440) Gg CH_3Cl yr^{-1} from coastal salt marshes (Rhew et al., 2000), 24 Gg $CHCl_3$ yr^{-1} and 35 Gg CH_3Cl yr^{-1} from peat land and freshwater wetland ecosystems (Dimmer et al., 2001), a global conifer forest floor source of 85 (39–131) Gg CH_3Cl yr^{-1}, and a global flux of 5.8 Gg CH_3Cl yr^{-1} from rice paddies. We assumed global biomass burning emissions of 909 Gg CH_3Cl yr^{-1} and 2 Gg $CHCl_3$ yr^{-1} according to Lobert et al. (1999) and an additional biomass burning source of 118 Gg CH_3Cl yr^{-1} from Asian biofuel use from Scheeren et al. (2002). Global annual emissions of ∼10 Gg CH_3Cl, 62±25 Gg $CHCl_3$, and 366±20 Gg C_2Cl_4 from industrial activities, 107±10 Gg CH_3Cl and ∼1.9 Gg C_2Cl_4 from fossil fuel combustion, and 45±33 Gg CH_3Cl from waste incineration for the year 1990 were taken from McCulloch et al. (1999a, b) and Aucott et al. (1999). We note that these emissions were estimated for the year 1990. McCulloch et al. (1999b) showed that the production and emission of industrial chlorocarbons is directly proportional to the economic activity. Industrial emissions for the year 2000, although not yet available, are probably somewhat higher than in 1990 due to the increased world economy over that decade.

We estimate a total annual CH_3Cl source flux of about 4 Tg (Table 4), which is in excellent agreement with the annual global sink of 4.0 Tg by Montzka et al. (2003). The annual source fluxes of 0.64 Tg $CHCl_3$ and 0.45 Tg C_2Cl_4 agree reasonably well (within the uncertainty) with their estimated annual global total sinks of 0.46 Tg and 0.51 Tg from Keene et al. (1999). The overestimation of the global annual source of 0.17 Tg $CHCl_3$ (+29%) is most likely mainly due to the highly uncertain ocean source estimate from Khalil et al. (1999). Although the missing source of 0.13 Tg C_2Cl_4 yr^{-1}, reported by Keene et al. (1999), can be reduced by half by our flux estimate from global forests, the budget of C_2Cl_4 remains to be unbalanced by −60 Gg.

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6. Decreasing trends in atmospheric CH_3Cl

In the literature, there exist two long-term CH_3Cl datasets from polar firn samples (Butler et al., 1999; Kasper et al., 2003) and one from atmospheric measurements (Khalil and Rasmussen, 1999). Khalil and Rasmussen (1999) present a record of CH_3Cl measurements from 1981 to 1997 from various background sites around the world. A compilation of these measurements suggests a weak decreasing trend of methyl chloride of the order of a few pptv per year over the last two decades. A similar trend was deduced from recent firn air analyses by Kaspers et al. (2003), who found a decrease of 1.2±0.6 pptv CH_3Cl per year (−0.2 ± 0.1% per year) between 1975 and 2000. In contrast, the measurements from Butler et al. (1999) suggest an increase of 5–10% in atmospheric CH_3Cl over the past century. Although we cannot explain this inconsistency, the majority of evidence suggests that CH_3Cl decreased over the last 20 years. Khalil and Rasmussen (1999) explained the global trend from a possible decrease of the OH-radical over the last 20 years reported by Krol et al. (1998) and later by Prinn et al. (2001). Recent work by Krol et al. (2003) has indicated however, that the previously reported negative OH trend in the 1990s seems to be unlikely and appears to be related to underestimated sources of methyl chloroform (1,1,1-trichloroethane) in global models. Methyl chloroform is used in global models to estimate the budget of the OH-radical since it has only anthropogenic sources and its main removal is by reaction with OH. Hence, in the absence of an OH trend, it appears that one or more sources of CH_3Cl have become smaller over the last two decades.

The main CH_3Cl sources are biomass burning, the oceans and tropical vegetation (see previous section). In a recent study on interannual and seasonal variability of biomass burning by Duncan et al. (2003), no apparent trend in biomass burning emissions over the last two decades was reported. When we perform a linear regression analysis on the global CO biomass burning emissions of CO (in Tg C yr^{-1}) as a function of time (in years), we can deduce a positive trend of the order of 0.6% per year (r = 0.55) between 1980 and 1997. Clearly, a biomass burning emission trend, if any,

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is most likely not related to a decrease in CH_3Cl. In addition, there are no studies indicative of any long-term trend in oceanic emissions. There is, however, significant evidence that the oceans have warmed up over the last 40 years due to the increase of greenhouse gases in the atmosphere (Barnett et al., 2001; Levitus et al., 2001). This suggests that the release of CH_3Cl from the oceans could have increased over that period. Although significant for the earth climate system, the global mean sea-surface temperature rise was less than 1°C over the last century (Levitus et al., 2001). Therefore, we consider the temperature effect on oceanic CH_3Cl emissions over the last 20 years to be negligible.

Based on this and other work (Lee-Taylor et al., 2001; Yokouchi et al., 2002) we find that the largest source of CH_3Cl is emissions from tropical vegetation. The latest estimates of global forest area cover by the FAO (FAO, 2001) show that the amount of tropical forest has decreased from 210.4×10^7 ha in 1980 to 179.1×10^7 ha in the year 2000 (corrected for replanted forest area), which equals a decrease of $-0.74\%\,yr^{-1}$. The trends of CH_3Cl, biomass burning and tropical forest cover are presented in Fig. 8. The extrapolated CH_3Cl trend between 1980 and the year 2000 is -1.3 pptv yr^{-1} or -0.2% yr^{-1} ($r = 0.67$). Hence, we propose that the strong decrease of tropical forest cover from anthropogenic activities over the last two decades could explain the observed decrease in global mean methyl chloride. In order to test the relationship between CH_3Cl and tropical forest cover more quantitatively, we assume that the yearly global mean atmospheric CH_3Cl concentration $[CH_3Cl]_t$ (of the year t) is composed of the relative fractions (in pptv) of the major sources:

$$[CH_3Cl]_{t_0} = ((1-n_a\Delta t)(S_a/\sum S) + (1-n_b\Delta t)(S_b/\sum S) + \ldots) \times [CH_3Cl]_{t_1}, \quad (4)$$

where $(1 - n_a\Delta t)$ is the relative annual trend n of source a over a period Δt denoting the number of years between the year t_0 (1980) and t_1 (2000); $(S_a/\sum S)$ is the fraction of source S_a relative to the sum of all sources $\sum S$.

We assume that global emissions from oceans, wetlands as well as the relatively small contribution from industrial emissions of CH_3Cl remained constant over the last

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two decades. For the reference year 2000 we can calculate a $[CH_3Cl]_{2000}$ of 543 (±16) pptv (the measured variability is ±3% yr^{-1}) based on the trend in the Khalil and Rasmussen (1999) data set shown in Fig. 7. Applying a linear trend back in time of −0.6% yr^{-1} for the biomass burning fraction and of +0.74% yr^{-1} for the fraction of tropical forests, we can then calculate a $[CH_3Cl]_{1980}$ of 566 pptv (Table 5). This value compares very well with the $[CH_3Cl]_{1980}$ of 567 (±17) pptv based on the observed trend and shows more quantitatively that the clearing of tropical forest can explain the observed decrease of the global mean CH_3Cl concentration. Clearly, our hypothesis implies that the atmospheric CH_3Cl concentration could have varied strongly in the geological past as a function of climate variability and global forest cover.

7. Summary and conclusions

We have presented measurements of reactive chlorocarbons CH_3Cl, CH_2Cl_2, $CHCl_3$ and C_2Cl_4 in the boundary layer and free troposphere over Surinam during March 1998. The horizontal and vertical distributions have been analyzed with the help of concurrent measurements of CO, CH_3CN, and non-methane hydrocarbons, as well as with 10-day back-trajectories. The vertical profiles show enhanced concentrations in the boundary layer and in the free troposphere between 8–12 km. We find that the free troposphere above 8 km altitude was strongly affected by deep convective outflow associated with the ITCZ, which was located a few degrees south of Surinam. Polluted air masses containing enhanced chlorocarbons appear to originate over the populated northwestern part of Brazil. High CH_3Cl concentrations correlating with relatively low CO, CH_3CN and C_2–C_6 NMHCs seem to come from the Central Amazonia pointing to biogenic sources.

We found a significant positive gradient of the CH_3Cl, $CHCl_3$ and C_2Cl_4 concentration in the mixing layer between the Surinam coast and the Brazilian border at 6° S. No correlation of CH_2Cl_2 with latitude was found. These gradients point to significant biogenic sources and corroborate the findings of Yokouchi et al. (2002). The change of

chlorocarbon concentration as a function of air mass residence time over the rainforest was used to calculate an emission factor in pptv h^{-1}. For this we used a selection of the data, representing air masses not affected by local biomass burning emissions or urban/industrial pollution. With these emission factors we could calculate fluxes of 7.6 ± 2.7 μg CH_3Cl m^{-2} h^{-1}, 1.11 ± 0.22 μg $CHCl_3$ m^{-2} h^{-1}, and 0.36 ± 0.067 μg C_2Cl_4 m^{-2} h^{-1}, representative for the Surinam tropical rainforest ecosystem. Hence, these fluxes encompass emissions from microbiological soil processes, fungal decomposition of wood, as well as direct emission from plants. Extrapolating these fluxes onto a continental scale and using the FAO 2000 tropical forest cover estimates (FAO, 2001), we can estimate annual emission fluxes from the Amazon tropical rainforest of 0.544 Tg CH_3Cl yr^{-1}, 0.079 Tg $CHCl_3$ yr^{-1}, and 0.026 Tg C_2Cl_4 yr^{-1}. The total emission flux estimates from tropical rainforests in South-America, Asia and Africa applying the Surinam flux value and the flux value from Yokouchi et al. (2002) for Asian highland tropical forest add up to 2 Tg CH_3Cl yr^{-1}. This value compares well with the model estimate of 2.3 Tg yr^{-1} by Lee-Taylor et al. (2001) and can account for the remaining missing sources in the CH_3Cl budget. Our estimate of an annual flux of ~57 Gg C_2Cl_4 yr^{-1} from global forest ecosystems can account for half of the previously missing sources in the budget by Keene et al. (1999).

The important role of tropical vegetation in the global budget of CH_3Cl indicates that changes in tropical forest cover could affect the atmospheric concentration. Indeed, we show that there are strong indications that the reduction of tropical forest area over the past 20 years can largely explain the downward trend in atmospheric CH_3Cl observed by Khalil and Rasmussen (1999) and Kaspers et al. (2003).

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Table 1. Overview of the mean $\pm 1\sigma$ standard deviation and median (between parenthesis) trace gas concentrations in the mixing layer (ML), the lower free troposphere (LT), and the middle free troposphere (MT). The number of canister samples is denoted by *N*

Species	ML-mean (median) < 2 km alt. *N* = 42	LT-mean (median) 3–7 km alt. *N* = 12	MT-mean (median) 7–12 km alt. *N* = 26
CO ppbv	131±11 (134)	119±12 (117)	125±29 (120)
CH_3CN pptv	192±83 (183)	201±65 (207)	143±68 (133)
C_2H_6 pptv	837±193 (769)	630±87 (610)	778±346 (658)
C_2H_2 pptv	86±31 (78)	95±44 (97)	120±72 (111)
C_3H_8 pptv	92±31 (81)	64±23 (60)	89±59 (66)
$n-C_4H_{10}$ pptv	15±5 (15)	18±11 (17)	19±10 (19)
C_6H_6 pptv	30±17 (26)	24±9 (27)	57±50 (41)
CH_3Cl pptv	624±36 (628)	640±31 (630)	635±51 (636)
CH_2Cl_2 pptv	26.0±2.9 (26.2)	16.4±0.3 (16.4)	16.3±4.4 (17.5)
$CHCl_3$ pptv	9.2±2.3 (9.0)	6.6±1.7 (6.5)	6.9±3.5 (6.3)
C_2Cl_4 pptv	3.8±1.3 (3.5)	4.3±2.5 (3.9)	4.4±3.0 (3.2)

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Table 2. Emission factors of chlorocarbons as a function of the FCT, ΔC/ΔFCT in pptv h^{-1}. The number of measurements is denoted by *N*. The correlation coefficient, *r*, is given at the 95% confidence limit

Species	ΔC/ΔFCT	*N*	*r*
CH_3Cl	2.62±0.61	27	0.58
$CHCl_3$	0.161±0.011	26	0.83
C_2Cl_4	0.038±0.006	24	0.48

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Table 3. Overview of mean flux estimates in μg m^{-2} h^{-1} for CH_3Cl and $CHCl_3$ from forest sources. Uncertainty (1σ standard deviation) or range is given between parentheses

Species	Flux	Forest source	Reference
CH_3Cl	3.9 (2.1)	Irish conifer forest soil	Dimmer et al. (2001)
	5.4 (3.8–8)	Glasshouse tropical forest	Yokouchi et al. (2002)
	7.6 (1.8)	Surinam rainforest	This work
	53 (12)	Tropical coastal land (Okinawa island)	Li et al. (1999); Yokouchi et al. (2000)
$CHCl_3$	0.033 (0.003–0.2)	Danish spruce forest soil	Haselmann et al. (2000a)
	0.11 (0.05–0.12)	Dutch fir forest soil	Hoekstra et al. (2001)
	0.34 (0.970.77)	Wood chips covered soil	Hoekstra et al. (2001)
	1.11 (0.08)	Surinam rainforest	This work
	8.6 (8.2)	Irish conifer forest soil	Dimmer et al. (2001)
C_2Cl_4	0.022 (0.008–0.04)	Dutch fir forest soil	Hoekstra et al. (2001)
	0.36 (0.067)	Surinam rainforest	This work

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Table 4. Global source and sink budgets of CH_3Cl, $CHCl_3$, and C_2Cl_4 in the troposphere in Tg yr^{-1}

Sources	CH_3Cl	$CHCl_3$	C_2Cl_4	Reference
Amazon forest	0.544	0.079	0.026	this work
Asian lowland forest	0.882			Yokouchi et al. (2002)
		0.013	0.004	this work
High Asian tropical forest	0.090	0.013	0.004	this work
Other tropical forest	0.484	0.070	0.023	this work
Temperate forest soil		0.0054		after Haselmann et al. (2000a)
			0.0036	after Hoekstra et al. (2001)
Conifer forest soil	0.085			Dimmer et al. (2001)
Oceans	0.477			Lee-Taylor et al. (2001)
		0.36	0.019	Khalil et al. (1999)
Coastal salt marches	0.17			Rhew et al. (2000)
Wetlands (incl. Peatbog)	0.035	0.024		Dimmer et al. (2001)
Rice paddies	0.006			Redeker et al. (2000)
Biomass burning	0.909	0.002		Lobert et al. (1999)
Asian biofuel emissions	0.118			after Scheeren et al. (2002)
Industry	0.010	0.069	0.366	McCulloch et al. (1999)
Waste incineration	0.045			McCulloch et al. (1999)
Fossil fuel combustion	0.107		0.0019	McCulloch et al. (1999)
All sources	3.96	0.63	0.45	
All sinks	4.00			Montzka et. (2003)
		0.46	0.51	Keene et al. (1999)
Sources – Sinks	−0.04	0.17	−0.06	

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Table 5. Contribution of different sources (in pptv) to the global mean CH_3Cl concentration in the year 2000 (trend) and the year 1980 (extrapolated)

Year	f(forests)	f(biomass burning)	f(oceans & wetlands)	f(industry & waste burning)	[CH_3Cl]
2000	286	141	93	23	543
1980	326	124	93	23	566

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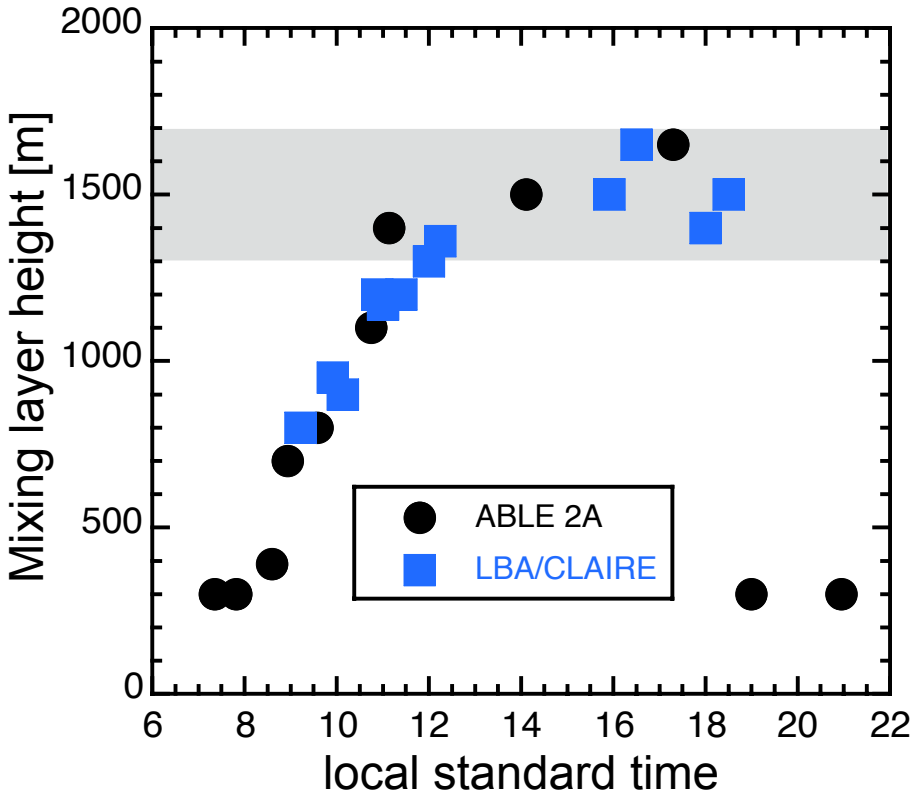

Fig. 1. Typical mixing layer heights over the Amazon rainforest during the dry season based on observed (potential) temperature inversions. The black dots are based on balloon and rawisonde profiles made during the ABLE 2A campaign (July 1985, Manaus region, Central Amazonia). The blue squares refer to temperature profiles obtained during March 1998 over the Surinam rainforest from ascents and descents with the Citation. The gray band denotes the range of mixing layer heights corresponding with the Surinam boundary layer measurements.

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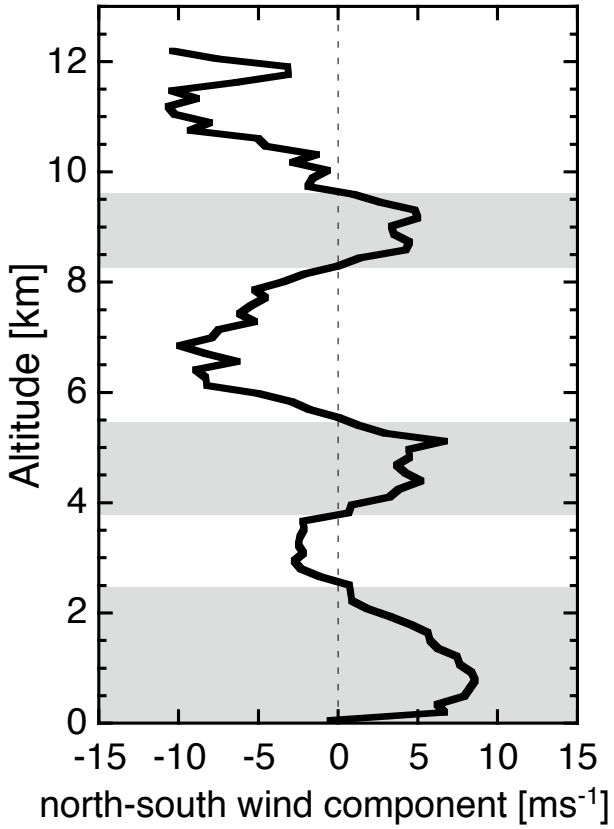

Fig. 2. Mean vertical wind profile showing the north-south wind component as cos(WA) × WS in m s^{-1}. Gray areas denote northerly winds.

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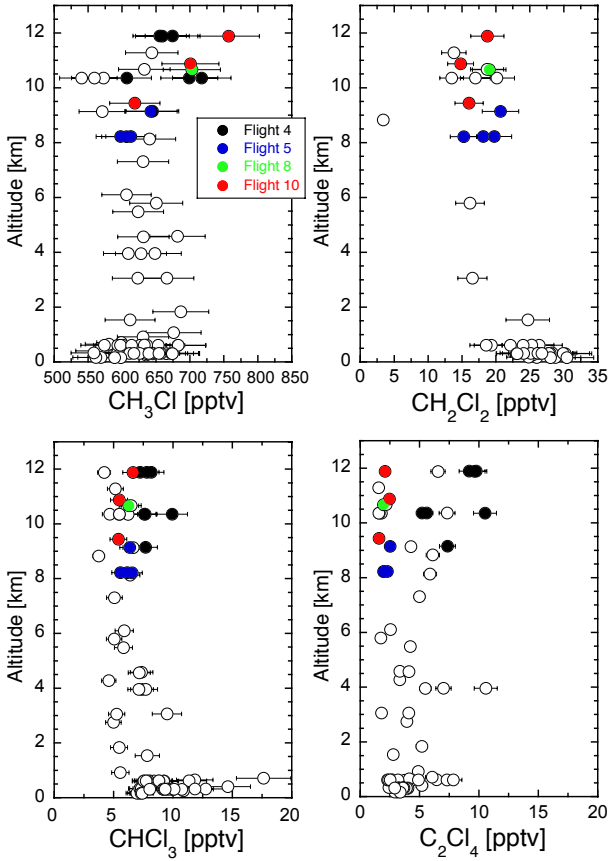

Fig. 3. (a) Vertical profiles of selected chlorocarbons (a) and combustion tracers (b). Error bars denote the measurement uncertainty. Color coding refers to the flights where outflow from the ITCZ has been observed in the FT between 8 and 12 km altitude.

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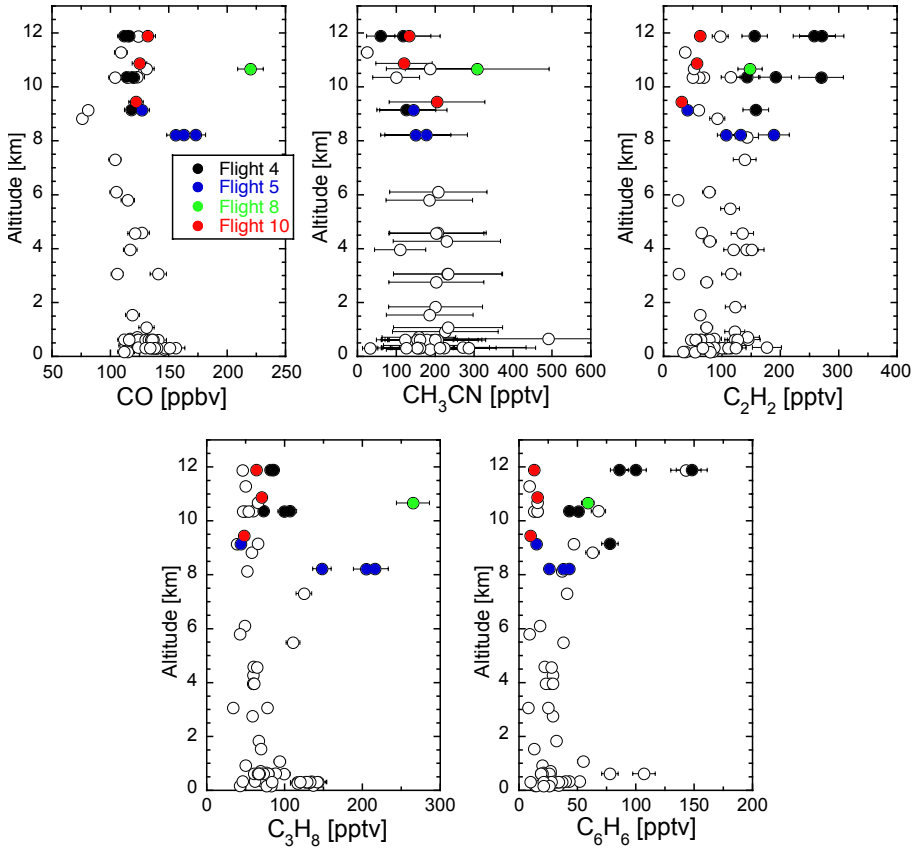

Fig. 3. (b) Continued.

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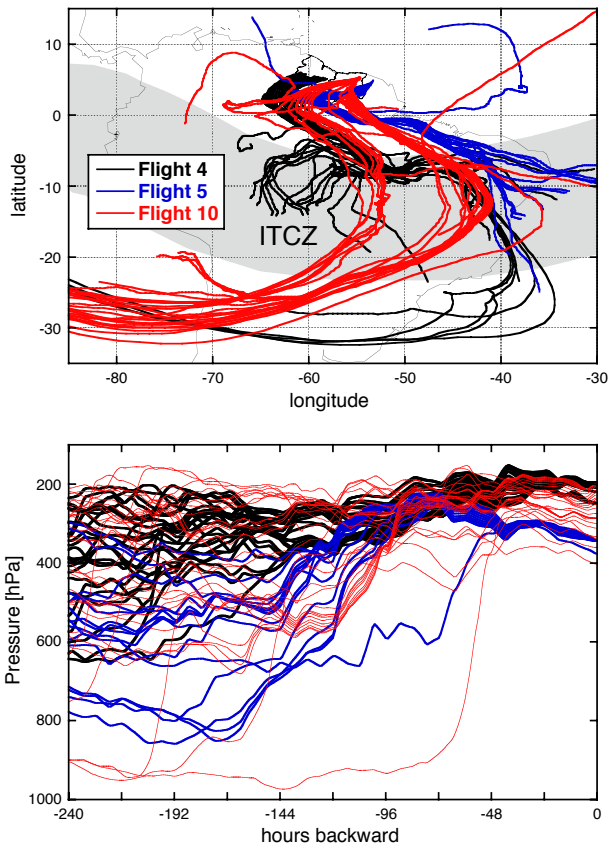

Fig. 4. Overview of 10-day back-trajectories based on ECMWF wind fields starting in the UT along the flight track of flight 4 (19 March), flight 5 (21 March) and flight 10 (29 March). The top plate (as a function of latitude and longitude) shows a predominant southwesterly air mass origin. The bottom plate (as a function of pressure and time) shows several events of fast upward transport associated with the ITCZ.

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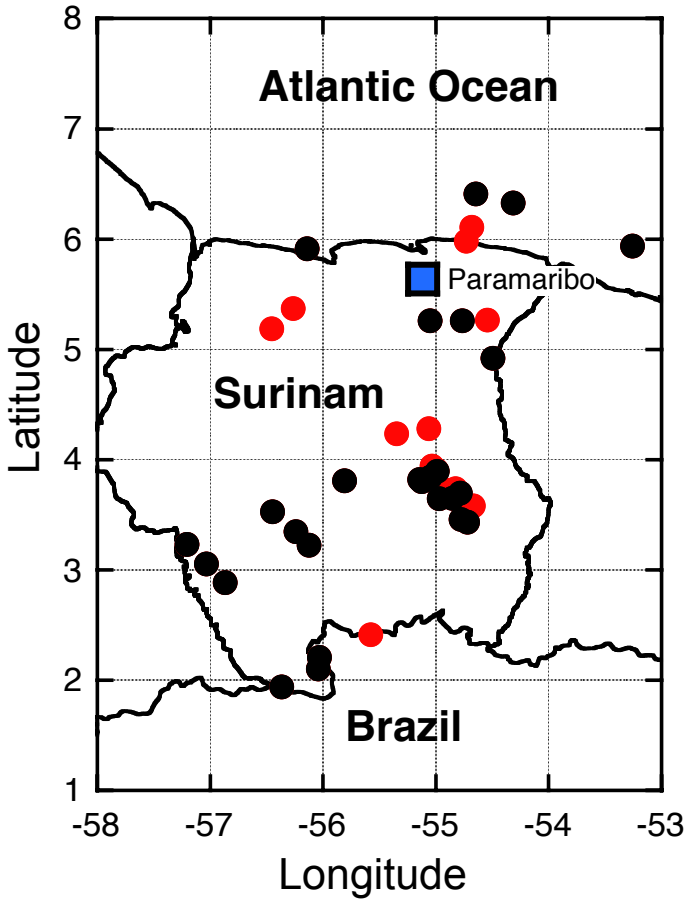

Fig. 5. Geographical distribution of the air samples (dots) collected in the Surinam boundary layer. The black dots are the samples selected for the flux analysis. The blue square denotes the location of Paramaribo, the capital of Surinam.

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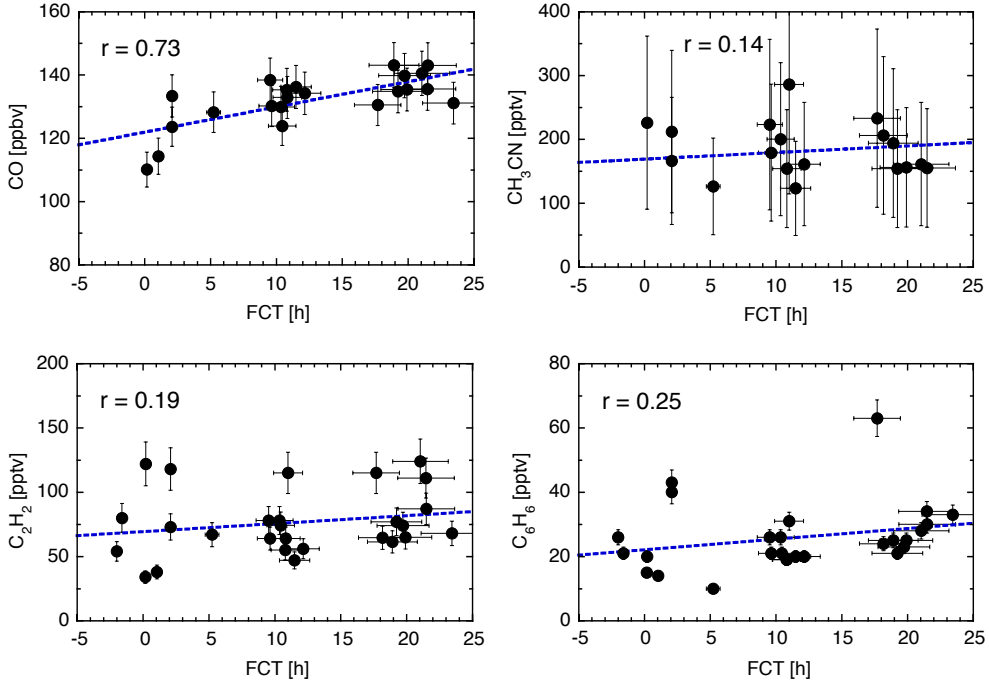

Fig. 6. (a) The concentration of combustion species (a) and halocarbons (b) as a function of the air mass Forest Contact Time (FCT) in hours (h) in the mixing layer over the Surinam rainforest. Error bars denote the uncertainty.

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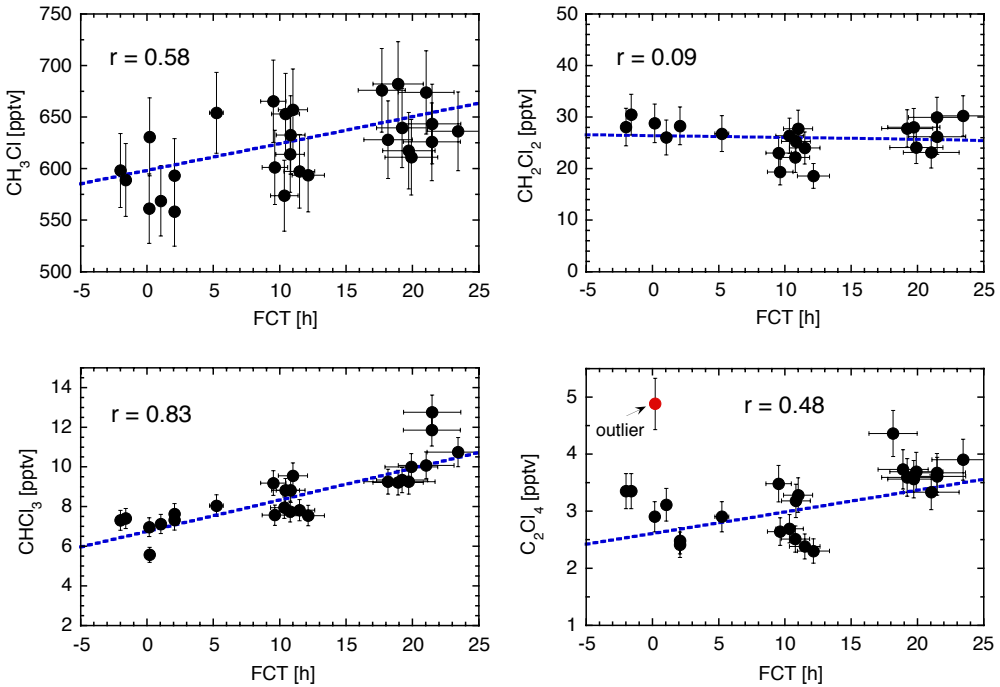

Fig. 6. (b) Continued.

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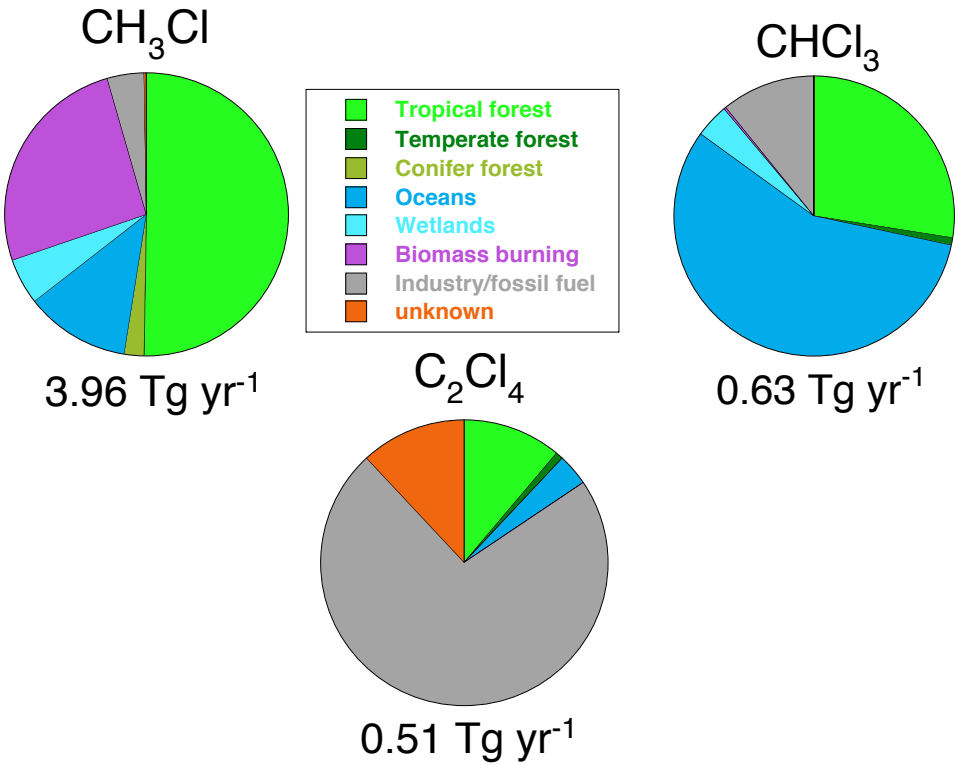

Fig. 7. Pie plots showing the composition of global source budgets of CH_3Cl, $CHCl_3$ and C_2Cl_4 according to present knowledge.

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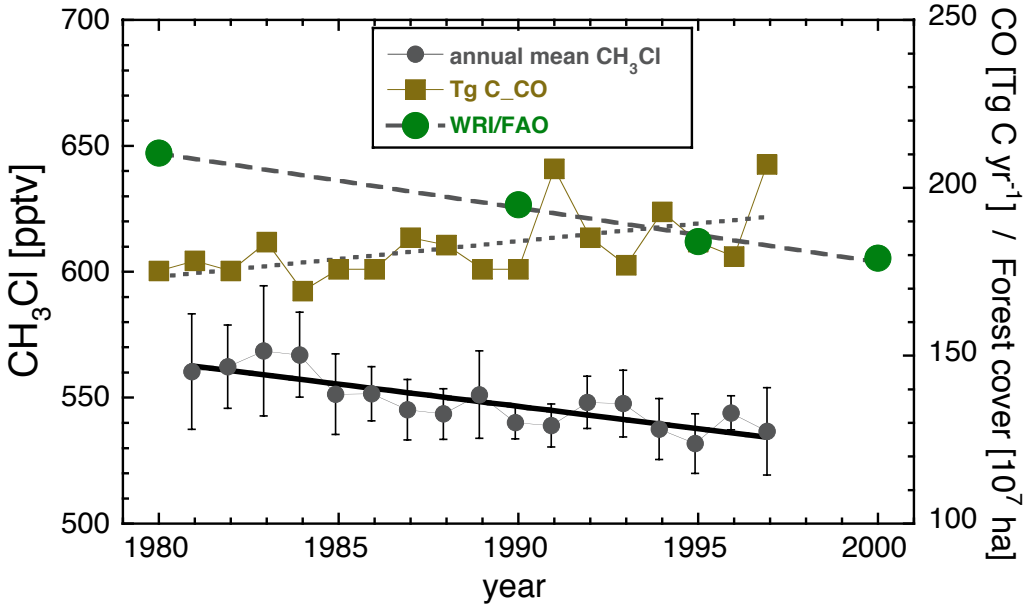

Fig. 8. Global trends of atmospheric CH_3Cl (data from Khalil and Rasmussen, 1999), tropical rain forest area cover (FAO, 2001), and global biomass burning emissions (Duncan et al., 2003) between the year 1980 and 2000. The error bar in the CH_3Cl data denotes the 1σ standard deviation of the yearly mean. We note that the Khalil and Rasmussen (1999) CH_3Cl data have been scaled down by a factor of 0.916, according to recommendations by Montzka et al. (2003).

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